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(54) Title: THERMOCHROMIC INK COMPOSITION, AND ARTICLE MADE THEREFROM

(57) Abstract: An article, such as a tamper evident container, includes a thermochromic ink composition comprising a leuco dye, a source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydroxylated poly (vinyl acetate), and an organic compound having at least one carbonyl group. The ink composition is characterized by improved wet abrasion resistance.

**THERMOCHROMIC INK COMPOSITION, AND ARTICLE MADE THEREFROM**

This application claims the benefit of U.S. Provisional Application No. 60/143,211, filed July 9, 1999.

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**Field Of The Invention**

The present invention relates to a thermochromic ink composition, and to articles, more particularly to tamper evident containers such as tamper evident envelopes, made therefrom, characterized by improved wet adhesion to a substrate, and improved  
10 wet abrasion resistance, in which a visible indication is provided if an attempt is made to gain access to the contents of the tamper evident container.

**Background Of The Invention**

It is known for banking establishments and the like to use tamper evident containers for transmitting valuables, for example specified sums of money, securities, cash  
15 in transit (CIT), etc. from one department to another. The system operated by such establishments is such that it is readily possible to ascertain whether a tamper evident container has been stolen in transit. However it is ordinarily more difficult to ascertain whether the tamper evident container has been opened in transit and then resealed after  
20 some of the contents have been removed. In order to overcome this problem, tamper evident containers have been provided wherein any attempt to gain access to the interior of the tamper evident container becomes visibly apparent.

Typically, the walls of such tamper evident containers are formed of sheet material including a portion having an opening which gives access to the interior of the tamper evident container. The tamper evident containers include a closure portion arranged  
25 to be superposed on the portion having the opening, to close the tamper evident container. Closure is effected by means of a band of high-tack adhesive which is applied across the closure portion or the portion having the opening, for example from the molten state, from transfer tape, solvent cast or in the form of a tape. The adhesive may be  
30 pressure sensitive adhesive, and suitable adhesives include thermoplastic hot melt adhesives, silicone adhesives, acrylic pressure sensitive adhesives, solvent cast adhesives, UV (ultraviolet) or EB (electron beam) cured acrylic adhesives, and the like.

Such adhesives are required to have high initial tack with respect to the surface of the sheet material and also to have high adhesive and cohesive strength. In order to  
35 provide a visible indication of any attempt to open the tamper evident container by sepa-

rating the closure portion and the portion having the opening, the adhesive should be strong enough to cause stretching, tearing, or other distortion of the portions upon attempted opening of the container. If desired, perforations or serrated edges may be provided in the closure portion to indicate tearing and emphasize the effect.

5           With the exception of silicone adhesives, adhesives suitable for the closure of tamper evident containers have a softening temperature which is below the melting point of the closure portion and of the sheet material. The softening temperature is commonly in the range of between 50°C and 90°C. Accordingly, by the local application of heat, an unauthorized person can open and reseal the tamper evident container without any visible indication that the tamper evident container has been opened.

10           To discourage this practice, thermochromic inks have been used in tamper evident containers. These inks are formulated to develop a permanent, non-reversible, and visibly evident color change when the adhesive on the envelope is exposed to heating. In this way, if unauthorized access to e.g. a tamper evident container is attempted by means of local application of heat to an adhesive on the envelope, a color change in the ink makes this evident. Typical conventional thermochromic inks for this application are formulated from a leuco dye, a phenolic compound, an organic diluent, water, and polyvinyl alcohol.

          However, two problems arise when using such inks.

20           First, these inks typically exhibit poor adhesion to substrates such as polyethylene films. This is a significant problem in that polyolefinic substrates are otherwise useful materials for tamper evident containers, offering relatively low material cost, printability, and durability, and either transparency or opacity as desired.

          Second, this ink exhibits relatively poor wet abrasion resistance once the ink has been applied, e.g. by coating or printing, to the polymeric substrate.

25           It is therefore desirable to provide a thermochromic ink, and articles such as tamper evident containers which utilize such ink, which offer improved adhesion to polymeric substrates such as polyethylene films, and improved wet abrasion resistance to the dried ink.

30           The present invention offers such improvements by providing a thermochromic ink composition that includes a leuco dye; a source of labile hydrogen such as a phenolic compound; an organic diluent such as an ester; water; polyvinyl alcohol (PVOH); hydrolyzed poly(vinyl acetate) (herein "PVAc"); and an organic compound having at least one carbonyl group, such as an aldehyde.

### Summary Of The Invention

In a first aspect, a tamper evident container comprises a first portion; an opening in the first portion capable of providing access to the interior of the tamper evident container; a closure portion arranged to be superposable with the first portion; an adhesive, applied to the first portion or closure portion, having a free surface so arranged as to seal the opening on superposition of the first portion and the closure portion; and a thermochromic ink composition; wherein the thermochromic ink composition is disposed, on superposition of the first portion and the closure portion, adjacent to the opening; and wherein the at least one thermochromic ink composition comprises or is derived from a leuco dye, a source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydrolyzed poly (vinyl acetate), and an organic compound having at least one carbonyl group.

In a second aspect, a thermochromic ink composition comprises a leuco dye, a source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydrolyzed poly(vinyl acetate), and an organic compound having at least one carbonyl group.

In a third aspect, an article comprises a thermochromic ink composition, the composition comprising a leuco dye, a source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydrolyzed poly(vinyl acetate), and an organic compound having at least one carbonyl group.

In a fourth aspect, a method of making a thermochromic ink comprises combining a leuco dye, a source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydrolyzed poly(vinyl acetate), and an organic compound having at least one carbonyl group.

All compositional percentages used herein are presented on a "by weight" basis, unless designated otherwise.

### Definitions

"Container" herein refers to bags, pouches, envelopes, or other articles which can store a product.

"Thermochromic" herein refers to an ink that exhibits a permanent, non-reversible, and visibly evident color change when exposed to heat.

### Brief Description Of The Drawings

A detailed description of preferred embodiments of the invention follows, with reference to the attached drawings, wherein:

FIG. 1 is a diagrammatic front view of an open tamper evident container in accordance with a first embodiment of the present invention;

Figure 2a is a diagrammatic section through a part of the tamper evident container of Figure 1 on an increased scale when the tamper evident container is open;

5        Figure 2b is a diagrammatic section through a part of the tamper evident container of Figure 1 when the tamper evident container is closed;

Figure 3a and 3b are respectively diagrammatic sections through a variation of the tamper evident container of the embodiment of Figure 1 when open and closed;

10        Figure 4 is a diagrammatic section through a part of a tamper evident container of a second embodiment of the invention;

Figure 5 is a diagrammatic section through a variation of the tamper evident container of Figure 4 showing optional additional security features;

15        Figure 6 is a diagrammatic section through a precursor of a tamper evident container of the first embodiment of the invention when the tamper evident container is open, during an exemplary production process;

Figure 7 is a diagrammatic section through a tamper evident container of a third embodiment of the invention;

Figure 8 is a diagrammatic section through a tape of a fourth embodiment of the invention;

20        Figure 9 is a diagrammatic section through a tape of a fifth embodiment of the invention;

Figure 10 is a diagrammatic section through a tamper evident container of a sixth embodiment of the invention;

Figure 11 is an enlarged view of a portion of Figure 7; and

25        Figure 12 is an enlarged view of a portion of Figure 10.

#### Detailed Description Of The Invention

Referring to Figures 1 and 2, the tamper evident container is preferably formed from a single strip 1 of flexible thermoplastic sheet material. This sheet material can  
30        comprise any suitable material, preferably high density polyethylene, low density polyethylene, a blend of high density polyethylene and low density polyethylene, high density polyethylene with a filler, cellulose acetate, polyester, or polypropylene. For the sake of clarity, the sheet material is illustrated herein as a monolayer film. However, those skilled in the art will understand that multilayer films can also be beneficially used  
35        in connection with tamper evident containers. An example is a film with a polymeric

core or inner layer, and two outside layers of high density polyethylene. The sheet material is folded laterally along a fold line 2 to form a first portion 3 and a second portion 4. The thermoplastic sheet material is preferably transparent, partially transparent or translucent, or a combination of opaque and transparent so as to make it easier to see evidence of tampering. The folded portions 3 and 4 are heat welded to each other in a zone 5 which extends parallel with and close to each of the longitudinal and each of the lateral edges of the portions to produce a tamper evident container 6 wherein the second portion 4 is longer than the first portion 3. The second portion 4 has a closure portion in the form of a flap 7. The flap portion 7 is preferably at least translucent, and more preferably is transparent.

At an end region of the tamper evident container 6 closer to the flap portion 7, an opening line in the form of a slit 8 extends across the first portion 3 terminating at each end at the weld zone 5. The slit 8 provides access to the interior of the tamper evident container 6. A band of adhesive 9 is provided on the flap portion 7. The choice of adhesive is not limited, although the adhesive should be a high tack adhesive having high cohesive and adhesive strength, such that any attempt to open the tamper evident container by separating the first portion and the closure portion will result in stretching, tearing, or other distortion of the first and/or closure portions, and can include any or all of those adhesives mentioned above. The adhesive 9 may be applied from the molten state or in the form of a tape, or by any other suitable method such as solvent cast or transfer tape technique. As can be seen from Figure 2a, a releasable cover strip 10 is preferably provided to cover the free surface of the adhesive 9 when the tamper evident container is open.

An ink composition 11, comprising a band of a substance exhibiting a change of color, phase or state when subjected to heating, is provided on the flap portion 7 and is covered by the adhesive 9. The ink composition is visible through the flap portion 7.

When using the tamper evident container, the items to be held in the tamper evident container are introduced through the slit 8. The cover strip 10 is then removed from the adhesive 9 and the flap portion 7 is folded over onto the portion 3, with the fold line being close to the proximal laterally extending part of the weld zone 5. The disposition of the adhesive layer 9 relative to the fold line of the flap portion 7 is such that when the flap portion 7 is brought down onto the first portion 3, the part of the flap portion 7 carrying the adhesive 9 straddles the slit 8 so that the slit 8 is completely overlain by the said adhesive 9. Thus, the slit 8 is completely sealed and there is no access opening whatsoever to the interior of the tamper evident container 6 (see Figure 2b). Advanta-

geously, the parts of the first portion 3 adjacent to the slit 8 have previously been subjected to a surface treatment such as corona discharge to assist adhesion of the adhesive to the substrate. The ink composition 11 overlies at least that part of the portion 3 adjacent to the slit 8 which is distant from the lateral weld zone 5a. If desired, the flap portion 7 may include a receipt portion 12 which is detachable by means of perforations 13.

Referring to Figures 3a and 3b, in which parts corresponding to those of Figures 1 and 2 are indicated by like reference numerals, it will be seen that the ink composition can also be provided on at least that part of the portion 3 which is immediately adjacent the opening 8 distant from the lateral weld zone 5. After closure of the tamper evident container, the adhesive 9 completely overlies the opening slit 8 and the ink composition 11. In this embodiment, the adhesive 9 must be translucent, or preferably transparent, to ensure that the ink composition 11 is visible through the flap portion 7.

Referring to Figure 4, in which parts corresponding to parts in Figures 1 to 3b have the same reference numerals, the tamper evident container 66, which is shown in the open state, can be sealed by a closure member 14. The closure member 14 comprises a thermoplastic substrate 15 which is at least translucent and preferably is transparent and which is adhered to at least a part of the section 16 of the first portion 3 along the whole lateral width of the tamper evident container, and optionally to the second portion 4, by an adhesive layer 9. A releasable cover strip 10 prevents adhesion of the closure member 15 to the first portion 3 adjacent to the opening 8 prior to the filling of the tamper evident container. In use, the items to be held in the tamper evident container are introduced through the slit 8, the cover strip 10 is removed, and the closure member 14 seals the opening 8 by completely overlying the same. The free surface of the adhesive 9 which is exposed on removal of the cover strip 10 adheres the substrate 15 to the first portion 3, 16. An ink composition 11 is provided on the transparent thermoplastic substrate 15 in such a position that, when the tamper evident container is sealed, the ink composition overlies the opening 8, or at least that part of the first portion 3 which is adjacent to the opening 8 and distant from the lateral weld zone 5a. The ink composition 11 may equally be applied to the adhesive 9 (by for example ink jet printing) or to the part of the first portion 3 adjacent the slit opening 8 and distant from the weld zone 5a.

Further security features may be incorporated into the tamper evident containers as is particularly illustrated in Figure 5, which is a variation of the embodiment of Figure 4. These security features can also be incorporated into the embodiments of Figures 1 to 3. In Figure 5, the closure member 14 comprises a transparent thermoplastic substrate 15 which carries a discontinuous weakly bonded adhesive layer 17 such as ethyl cellulose and a strongly bonded adhesive layer 18 such as epoxy cellulose acetate propionate. Because of the layers 17 and 18,

any attempt to gain access to the interior of the tamper evident container 6 by lifting the substrate 15 will result in those parts of the layer 18 which are in registry with layer 17 remaining adhered to portions 3 and 4 whilst other parts of the layer 18 will remain adhered to substrate 15. This results in the formation of a visible pattern constituted by the split layer 18 which pattern cannot be obliterated by re-sealing the closure member. Soluble transparent or translucent dye may be carried in a layer 19. Layer 20 comprises a high tack adhesive in which the ink composition 11 is disposed. It is not essential, however, for the ink composition 11 to be disposed in the layer 20. Layer 21 is an optional second layer of adhesive which carries optional ink jet printing 22.

10 Referring now to Figure 6, the tamper evident container is produced by folding longitudinally a continuous length 101 of thermoplastic sheet material (after it has been optionally printed as appropriate) into a J-form where it includes a first portion 103 folded longitudinally at 102 so as to be superposed on a part of a second portion 104 so as to leave a flap portion 107 of the second portion 104 exposed. The first portion 103 is heat sealed to the second portion 15 104 by a longitudinally extending heat seal denoted by a reference numeral 105. Preferably, a longitudinally extending region of the flap portion 107, which region is generally parallel to the heat seal 105, is subjected to a surface treatment such as corona discharge to improve its adhesion characteristics in that region. A band of high-tack adhesive 109 is applied to that region and is covered by a removable cover strip 110 optionally after having been provided with 20 a security code by means of an ink jet printing technique. An ink composition 111 can be applied to the flap portion 107 prior to the application of the adhesive 109. Alternatively, the ink composition may be applied generally at region 113. The region indicated generally by 113 may also be subjected to a surface treatment such as corona discharge to improve its adhesion.

The continuous length 101 of sheet material is then cut transversely using a double 25 heat sealing device comprising two pairs of heat sealing jaws between which is located a cutting blade so that the sheet material is cut into adjacent transverse sections each having heat sealed edges. Each of these sections constitutes a tamper evident container in accordance with the invention. It will be appreciated that a similar method can be applied for the production of the tamper evident containers in accordance with Figures 4 and 5. It is particularly advantageous to apply the closure member as a pre-made tape which will desirably incorporate the ink composition. 30

Referring now to Figure 7, a tamper evident envelope includes a sheet portion 201 to which a tamper evident tape 203, having printed or coated thereon, or including as a layer thereof, the thermochromic ink of the invention, is adhered by means of seal 202. Seal 202 can 35 be e.g. a heat seal or an adhesive seal. Adhesive 205 is adhered to sheet portion 201, and is



covered by a removable release liner 204. Figure 11 is an enlargement of a portion of Figure 7. In practice, after a product such as cash, a biological specimen, or some other object is placed through the opening 211 into the interior of container 200, the release liner 204 is removed to expose adhesive 205. The tamper evident tape 203 is then pressed against adhesive 205 to seal the container. If an unauthorized attempt is made to open the container by heating the adhesive 205 of the container to reduce the level of adhesion of adhesive 205 to tamper evident tape 203, the tape 203 will change color.

Figure 10 illustrates an alternative embodiment. A tamper evident container 400 includes a sheet portion 401 to which a tamper evident tape 403, having printed or coated thereon, or including as a layer thereof, the thermochromic ink of the invention, is adhered by means of seal 402. Seal 402 can be e.g. a heat seal or an adhesive seal. Adhesive 405 is adhered to tamper evident tape 403, and is covered by a removable release liner 404. Figure 12 is an enlargement of a portion of Figure 10. In practice, after a product such as cash, a biological specimen, or some other object is placed through the opening 411 into the interior of container 400, the release liner 404 is removed to expose adhesive 405. The tamper evident tape 403, with adhesive 405 adhered thereto, is pressed against sheet portion 401 to seal the container. If an unauthorized attempt is made to open the container by heating the adhesive 405 of the container to reduce the level of adhesion of adhesive 405 to sheet portion 401, the tape 403 will change color.

Figures 8 and 9 illustrate two embodiments for either of tamper evident tape 203 or 403.

In Figure 8, a tape film 206 can be made of a clear or colored polymeric material such as a polyolefin. Adhered to a portion of tape film 206 is a layer of a tamper evident message print 207. This layer has a message printed thereon, generally masked by the tape film 206 and/or layer 208, which becomes visible and readable in the event someone seeks to gain access to the contents of the container by attempting to separate adhesive 205 or 405 from sheet material 201 or 401 respectively. Adhered to another portion of tape film 206 is a layer 209 of the thermochromic ink of the invention. Adhered to layer 207 is a layer 208 of an overcoat print. This layer, generally of a single opaque color, masks the message of the message print layer 207 unless and until the container is opened.

In Figure 9, a tape film 306 is made of a clear or colored polymeric material such as a polyolefin. Adhered to one side of tape film 306 is a layer 309 of the thermochromic ink of the invention. Adhered to the other side of tape film 306 is a layer of a tamper evident message print 307. This layer has a message printed thereon, generally masked by the tape film 306 and/or layer 308, which becomes visible and readable in the event someone seeks to gain ac-

cess to the contents of the container by separating adhesive 205 or 405 from sheet material 201 or 401 respectively. Adhered to layer 307 is a layer 308 of an overcoat print. This layer, generally of a single opaque color, masks the message of the message print layer 307 unless and until the container is opened. Adhesive layers 205 and 405 can each form a single or multiple band, and can form a straight, wavy, continuous, or discontinuous line pattern or design.

Likewise, thermochromic ink layers 209 and 309 can each form a single or multiple band, and can form a straight, wavy, continuous, or discontinuous line pattern or design.

#### Thermochromic Ink Composition

A leuco dye, a phenolic compound, organic diluent, water, and polyvinyl alcohol (PVOH) collectively comprise a conventional thermochromic ink.

A preferred ink, and one used in the examples to follow, is available from Tempil Company. The particular formulation has the product designation TIT-FWC-146. The formulation of this ink is believed to comprise:

#### Part A (40 to 60 % of ink)

a dye dispersion comprising:

11.2% leuco dye (COPIKEM™ 34)

48.5% polyvinyl alcohol (10% solution) (medium viscosity, 99% hydrolysis)

40.0% distilled water

0.3% nonionic surfactant (SURFYNOL™ TG)

and

#### Part B (60-40 % of ink)

an activator dispersion comprising:

12.0% Bisphenol A (from Shell Chemical)

7.7% organic diluent (e.g. wax such as stearamide or other fatty amides)

42.0% polyvinyl alcohol (10% solution) (medium viscosity, 99% hydrolysis)

38.0% distilled water

0.3% nonionic surfactant (SURFYNOL™ TG)

The dye and activator dispersions are ground separately and allowed to age for several hours. The two dispersions are then mixed together slowly with gentle stirring to form ink.

The leuco dye from which the present ink composition is made is available from BFG-Hilton Davis Inc. Examples of commercial leuco dyes suitable for use in the ink composition of the present invention are given in Table 1.

Table 1

Trade Name	Indicating Color*	Chemical Composition
COPIKEM™ 1	Blue	Crystal Violet Lactone
COPIKEM™ 5	Green	2'-di(phenylmethyl)amino-6'(diethyl amino) spiro(isobenzofuran-1(3H),9'(9H)xanthen)-3-one
COPIKEM™ 20	Magenta	3,3-bis(1-ethyl-2-methyl-1H-1H-indol-3-yl) 1-(3H)-isobenzofuranone
COPIKEM™ 34	Black	6'-(diethylamino)-3'-methyl-2'-(phenyl amino) spiro(isobenzofuran-1(3H),9'(9H)xanthen)-3-one

\* color to which the dye changes upon heating.

For the present invention, a source of labile hydrogen is preferably a phenolic compound such as phenol, Bisphenol A (4,4'-isopropylidenediphenol), resorcinol, catechol, hydroquinone, 1,2-bis(4-hydroxy phenyl) cyclohexane, dimyristyl phosphate, and/or zinc salt of Bisphenol A.

For the present invention, diluents which can be included in various amounts as needed in the thermochromic ink include organic diluents such as glycerol trimyristate, glycerol tri-  
laurate, octadecanol, tristearin, cetanol, triolein, and dilauryl adipate.

The inventors have found that hydrolyzed poly(vinyl acetate) (herein "PVAc") and an organic compound having at least one carbonyl group, preferably an aldehyde, more preferably a dialdehyde such as glyoxal, can be added to the conventional ink formulation to produce the ink composition 11 of the present invention.

In several replications of preparation of the thermochromic ink composition of the invention, the procedure was as follows.

Forty milliliters of conventional thermochromic ink as described above (Tempil TIT-FWC-146) was placed in a first beaker.

Ten milliliters of VINAC™ 210 polyvinyl acetate (PVAc) emulsion, available from Air Products, was placed in a second beaker.

Ten milliliters of Sigma G3140™ glyoxal (40% aqueous solution) available from Sigma was slowly added to the polyvinyl acetate emulsion of the second beaker by stirring. The addition of the glyoxal to the polyvinyl acetate emulsion took about ten minutes, and the mixture was then stirred for an additional two minutes. The PVAc-glyoxal mixture was then slowly added to the ink in the first beaker with continuous stirring of the ink. Addition of the PVAc-glyoxal mixture to the ink took between two and three minutes.

After addition of the PVAc-glyoxal mixture to the ink, the resultant ink composition was stirred for between four and five minutes.

The resultant ink composition was then applied to a polyolefin film in the form of a thin bead. A proofer (a rubber roll attached to a handle) was used to spread the bead of ink composition to form a thin film or coating. In some cases, a Mayer rod (a metering tool) was used to draw down or spread the bead into a thin film. The thin film of the ink composition was then allowed to dry at room temperature. In some cases, a hot air gun was set at a distance of two feet to blow warm air over the thin film. In such cases, the warm air stream was positioned horizontal to the film plane at a height of about one foot, with the warm air flowing essentially above and parallel to the film plane, and with a component of the warm air contacting the film surface. In a few cases, the film was dried in a hot air oven at 120°F for five minutes.

Although glyoxal was used in the working examples herein, alternative materials can be substituted for the glyoxal. These include other aldehydes, preferably dialdehydes, or other organic compounds having at least one and preferably at least two carbonyl groups. Preferred materials include formaldehyde (formalin), methyl glyoxal, succinal, glutyaldehyde, adipaldehyde, and the like.

#### Testing of Thermochromic Ink Composition (Wet Abrasion test)

A moistened paper towel was manually pressed firmly on the surface of the thin film of the ink composition and moved back and forth. An effort was made to keep the applied pressure constant. Failure was noted as the number of firm strokes required to show evidence of smearing or ink removal. Tamper evident container samples were fabricated substantially as described herein with respect to Figure 7 of the drawings, some with a band of the thermochromic ink composition of the present invention, and some control samples with a band of conventional thermochromic ink. These samples were tested using the wet abrasion test described above. The results of testing these samples are presented in Table 2.

Table 2

Example	No. of Rubs	Results
1	>15	The thermochromic ink composition of the invention, applied as a central stripe or band on a green tape, was not removed by the wet abrasion. Subsequent heating caused the stripe to turn color (turned to black).
2	>15	Same as Example 1.
3	>15	Same as Example 1.
4	>15	The thermochromic ink composition of the invention, applied so as to fully cover a green tape, was not removed by the wet abrasion. Subsequent heating caused the stripe to turn black.
Comparative 1	<2	A conventional thermochromic ink, printed as a repeating "X" on a green tape, was removed by the wet abrasion, resulting in a clear area in the right corner of the green tape.
5	>15	The thermochromic ink composition of the invention, coated on a yellow tape, showed poor uniformity of coating, but was not removed by the wet abrasion. Subsequent heating caused the stripe to turn black.
Comparative 2	<2	A conventional thermochromic ink, printed as a repeating "X" on a yellow tape, was removed by the wet abrasion, resulting in a clear area in the right corner of the tape.

Additional tamper evident container samples were hand drawn on a SHURTUFF® polyethylene substrate. Table 3 indicates the ratio of materials used in the thermochromic ink composition of the invention for each sample. The table also evaluates the results of testing these compositions by rubbing the band of ink with a moistened towel, as described above.

Table 3

Wet Adhesion performance of various Blends with TEMPIL™ Thermal Inks			
Sample Identification	No. of Rubs	Wet Adhesion rating	Thermal Performance (exhibited as color intensity)
FRANKLIN™(lab): TEMPIL™ 1:2	>15	Excellent	Excellent
FRANKLIN™(new): TEMPIL™ 1:2	<10	Good	Excellent
ELMERS™, SOBO™, LINECO™ and WELDBOND™ with TEMPIL™ 1:2	<10	Fair/Good	Excellent
VINAC™ 650: TEMPIL™ 1:2	<10	Good	Poor
VINAC™ 230: TEMPIL™ 1:2	<5	Poor	Poor
VINAC™ 210: TEMPIL™ 1:2	<5	Poor	Poor
VINAC™230:glyoxal:TEMPIL™ 1:1:4	>15	Excellent	Excellent
VINAC™210:glyoxal:TEMPIL™ 1:1:4	>15	Excellent	Excellent
PROGRESSIVE™: TEMPIL™ 1:2	<5	Poor	Poor
SOLUTIA™ TS-100: TEMPIL™ 1:2	<5	Poor	Poor
SOLUTIA™ TS-30: TEMPIL™ 1:2	<5	Poor	Poor

In Table 3, FRANKLIN™, ELMERST™, SOBOT™, LINECO™, WELDBOND™, VINACT™, PROGRESSIVET™, and SOLUTIA™ all refer to commercially available water-based glues containing hydrolyzed poly(vinyl acetate).

Thermochromic ink compositions of the present invention preferably comprise between 25% and 95%, more preferably between 40% and 90%, and most preferably between 60% and 85%, such as 80%, of the conventional thermochromic ink, and between 5% and 75%, more preferably between 10% and 60%, and most preferably between 15% and 40%, such as 20%, of the total of PVAc and organic compound having at least one carbonyl group.

The PVAc and organic compound having at least one carbonyl group are present in the thermochromic ink of the invention in a ratio (PVAc/organic compound) of preferably between 25/75 and 75/25, more preferably between 40/60 and 60/40, and most preferably at a ratio of 50/50.

Although the invention has been described herein primarily with respect to tamper evident containers such as security envelopes, the invention can also be beneficially used in connection with the packaging or containment of biological materials or specimens, test samples, DNA evidence, forensic or criminal evidence, or any other product or item requiring some protection against tampering, theft, substitution, destruction, etc.

Also, although the article of the invention has been described herein primarily as a tamper evident container such as a security envelope, other articles can also be beneficially made utilizing the thermochromic ink of the invention. These articles include labels, tapes, foam trays, air cushioning films, shrink and non-shrink films, laminates, and temperature indicators.

It is to be understood that variations of the present invention can be made without departing from the scope of the invention, which is not limited to the specific embodiments and examples disclosed herein, but extends to the claims presented below.

What is claimed is:

1. A tamper evident container comprises:
  - a) a first portion;
  - 5 b) an opening in the first portion capable of providing access to the interior of the tamper evident container;
  - c) a closure portion arranged to be superposable with the first portion;
  - d) an adhesive, applied to the first portion or closure portion, having a free surface so arranged as to seal the opening on superposition of the first
  - 10 portion and the closure portion; and
  - e) a thermochromic ink composition ;wherein the thermochromic ink composition is disposed, on superposition of the first portion and the closure portion, adjacent to the opening; and  
wherein the thermochromic ink composition comprises a leuco dye, a source of labile  
15 hydrogen, an organic diluent, water, polyvinyl alcohol, hydroxylated poly(vinyl acetate), and an organic compound having at least one carbonyl group.
2. The tamper evident container of claim 1 wherein the adhesive is disposed as a band on the first portion or closure portion.
- 20 3. The tamper evident container of claim 1 wherein the closure portion comprises a flap portion formed integrally with a portion of the sheet material of the tamper evident container.
- 25 4. The tamper evident container of claim 1 wherein the closure portion comprises a thermoplastic substrate to which the adhesive is applied, which substrate is affixed to the sheet material of the tamper evident container.
- 30 5. The tamper evident container of claim 4 wherein the thermoplastic substrate is affixed to the sheet material by means of an adhesive.
6. The tamper evident container of claim 4 wherein the thermoplastic substrate is heat welded to the sheet material.

7. The tamper evident container of claim 1 wherein a releasable cover-strip is provided on the free surface of the adhesive.
8. The tamper evident container of claim 1 wherein the ink composition is disposed on the closure portion.
9. The tamper evident container of claim 1 wherein the ink composition is disposed on the first portion.
10. The tamper evident container of claim 1 wherein the ink composition is disposed on the sheet material in a pattern or design.
11. The tamper evident container of claim 1 wherein the ink composition is such as to change colour at a temperature above that of normal use of the tamper evident container and below the melting temperature of the adhesive.
12. A thermochromic ink composition comprising:
- a) leuco dye;
  - b) a source of labile hydrogen;
  - c) an organic diluent;
  - d) water;
  - e) hydrolyzed poly(vinyl acetate); and
  - f) an organic compound having at least one carbonyl group.
13. The composition of claim 12 wherein the source of labile hydrogen comprises a phenolic compound.
14. The composition of claim 13 wherein the phenolic compound is selected from the group consisting of phenol, Bisphenol A (4,4'-isopropylidenediphenol), resorcinol, catechol, hydroquinone, 1,2-bis(4-hydroxy phenyl) cyclohexane, dimyristyl phosphate, and zinc salt of Bisphenol A.
15. The composition of claim 12 wherein the organic compound having at least one carbonyl group comprises an aldehyde.



16. The composition of claim 15 wherein the aldehyde is selected from the group consisting of glyoxal, formaldehyde (formalin), methyl glyoxal, succinal, glutyaldehyde, and adipaldehyde.
- 5 17. An article comprising a thermochromic ink composition, the composition comprising:
- a) a leuco dye;
  - b) a source of labile hydrogen;
  - c) an organic diluent;
  - 10 d) water;
  - e) hydrolyzed poly(vinyl acetate); and
  - f) an organic compound having at least one carbonyl group.
18. The article of claim 17 wherein the article comprises a label, tape, foam tray,  
15 air cushioning film, shrink film, non-shrink film, laminate, or temperature indicator.
19. The article of claim 17 wherein the source of labile hydrogen comprises a phenolic compound.
- 20 20. The article of claim 19 wherein the phenolic compound is selected from the group consisting of phenol, Bisphenol A (4,4'-isopropylidenediphenol), resorcinol, catechol, hydroquinone, 1,2-bis(4-hydroxy phenyl) cyclohexane, dimyristyl phosphate, and zinc salt of Bisphenol A.
- 25 21. The article of claim 17 wherein the organic compound having at least one carbonyl group comprises an aldehyde.
22. The article of claim 21 wherein the aldehyde is selected from the group consisting of glyoxal, formaldehyde (formalin), methyl glyoxal, succinal, glutyaldehyde, and  
30 adipaldehyde.
23. The article of claim 17 wherein the thermochromic ink composition is disposed on the article.

24. The article of claim 17 wherein the thermochromic ink composition is disposed in the article.

25. A method of making a thermochromic ink comprises combining a leuco dye, a  
5 source of labile hydrogen, an organic diluent, water, polyvinyl alcohol, hydrolyzed poly(vinyl acetate), and an organic compound having at least one carbonyl group.

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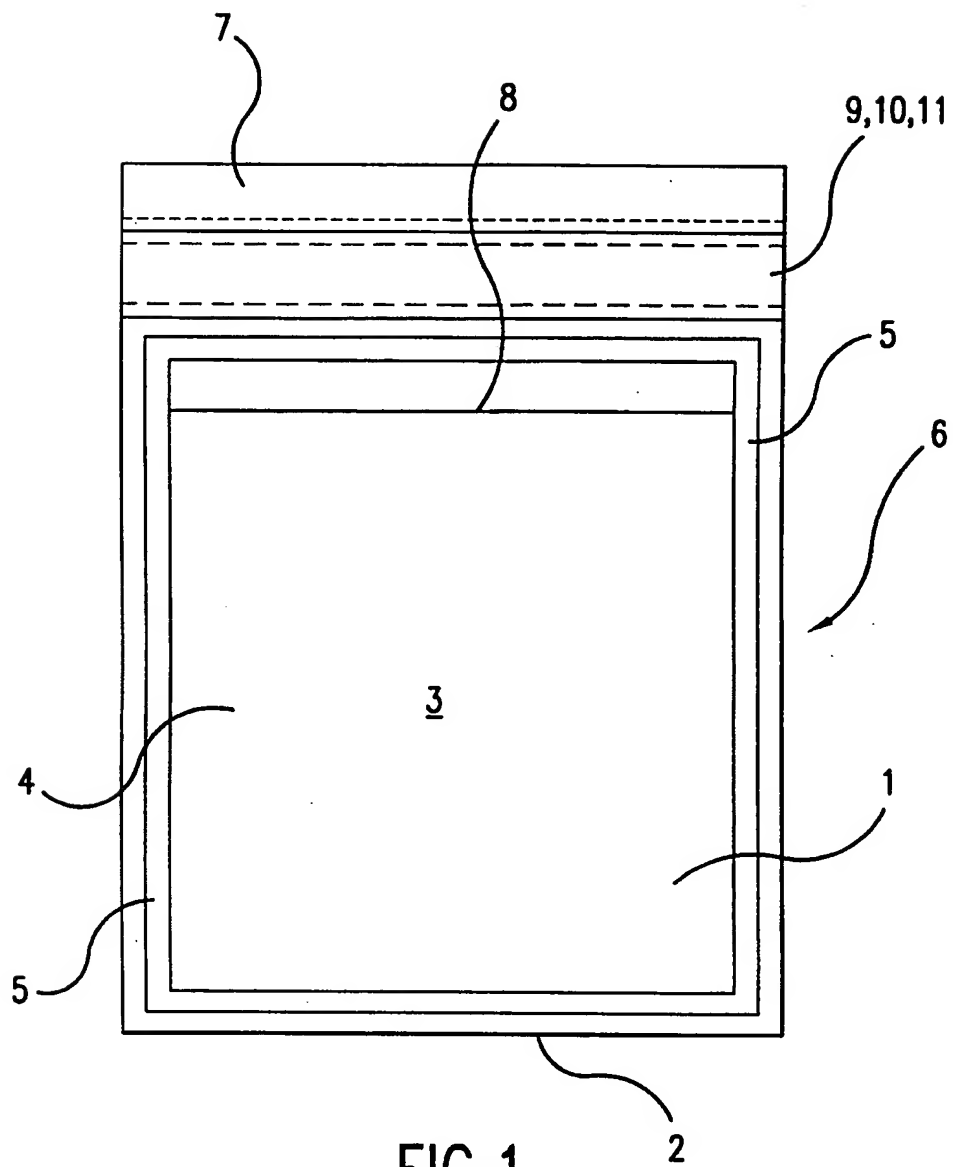


FIG.1

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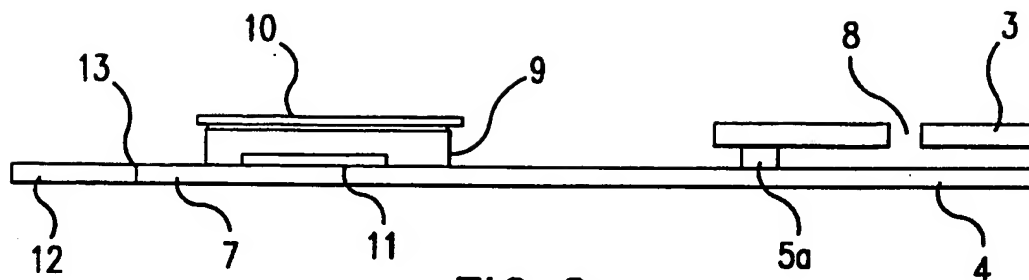


FIG. 2a

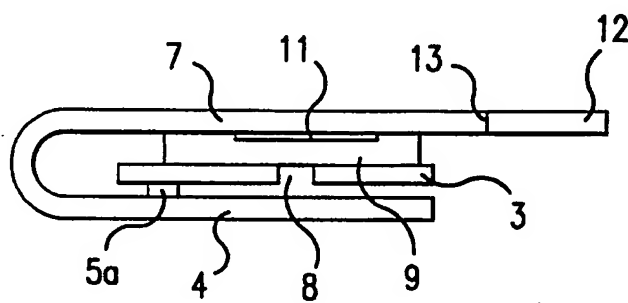


FIG. 2b

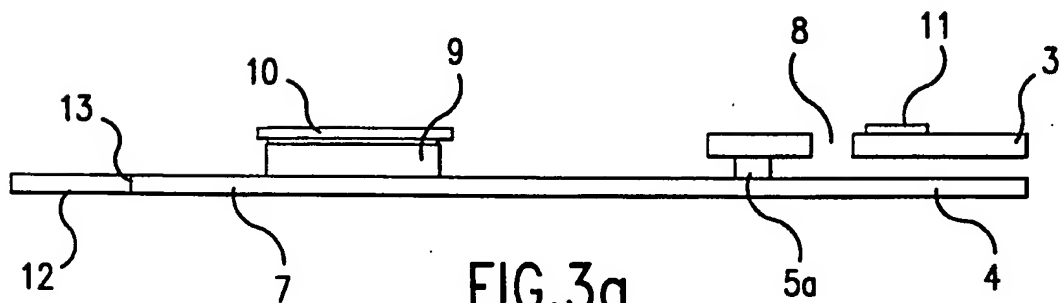


FIG. 3a

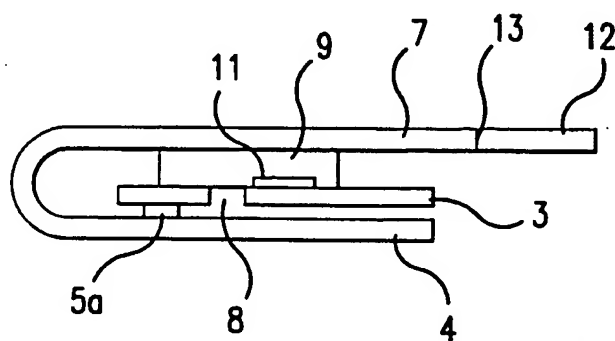


FIG. 3b

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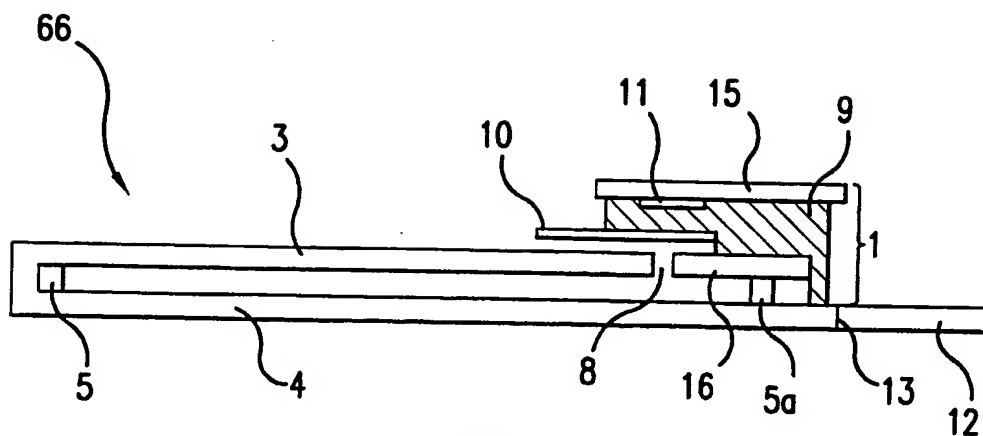


FIG. 4

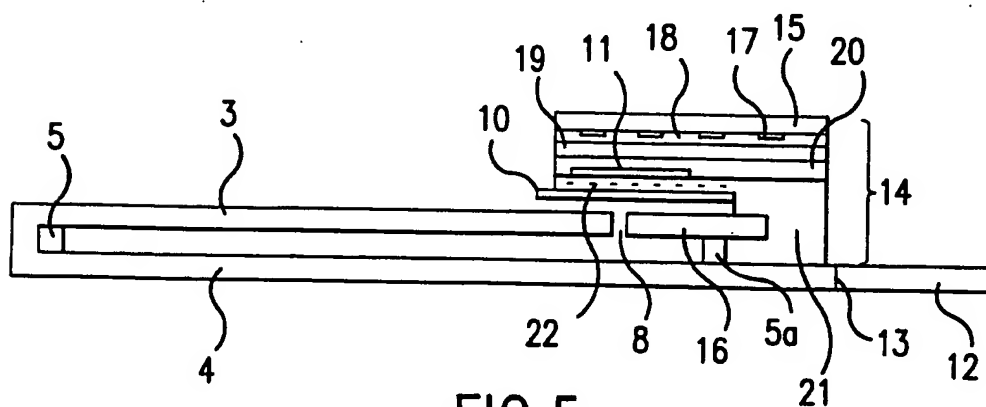


FIG. 5

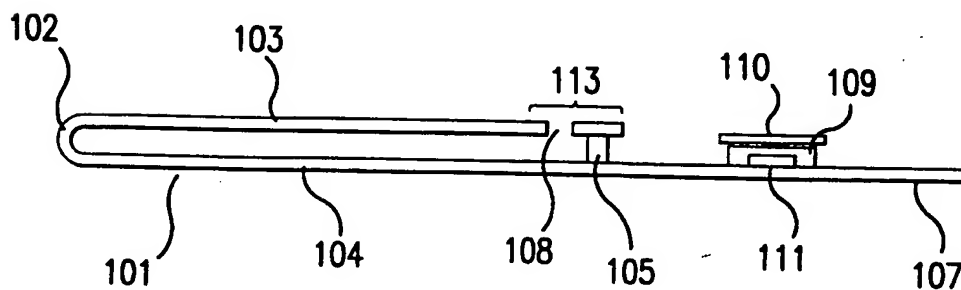


FIG. 6

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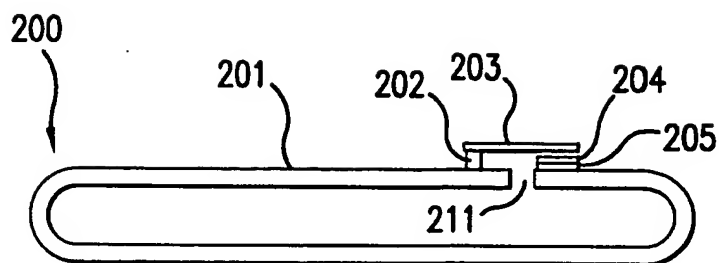


FIG. 7

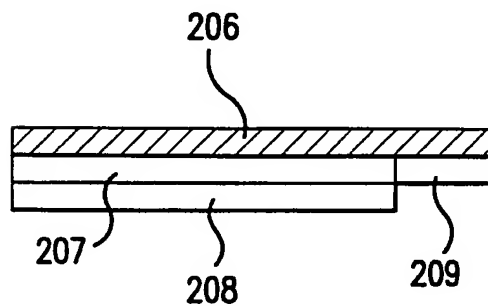


FIG. 8

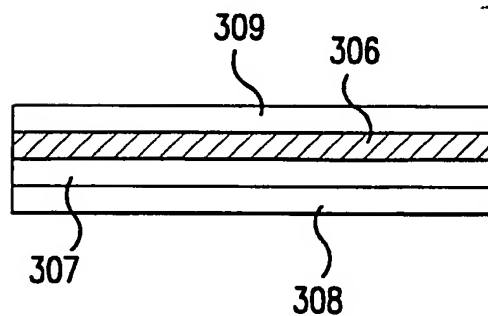


FIG. 9

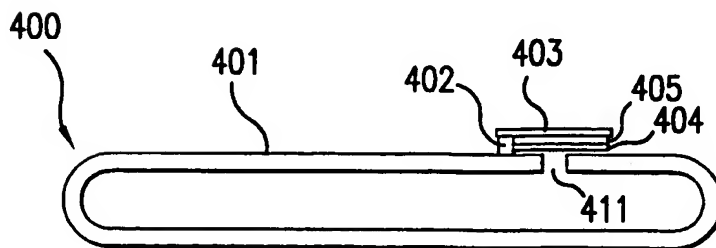


FIG. 10

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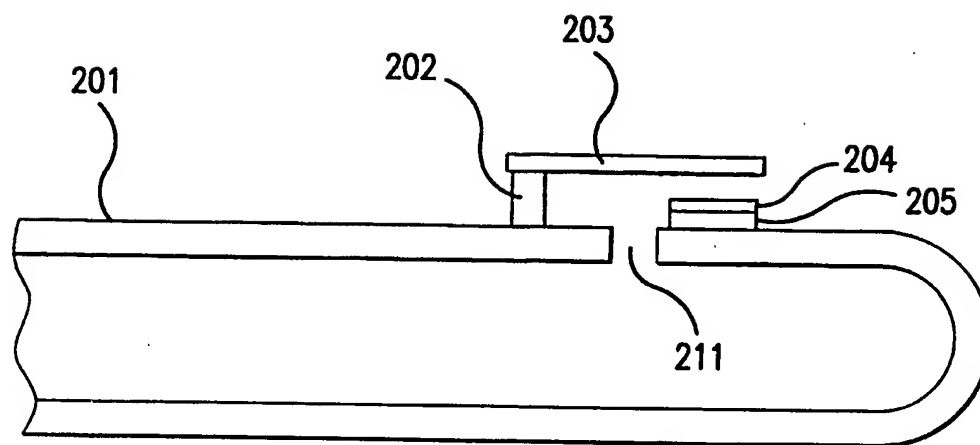


FIG. 11

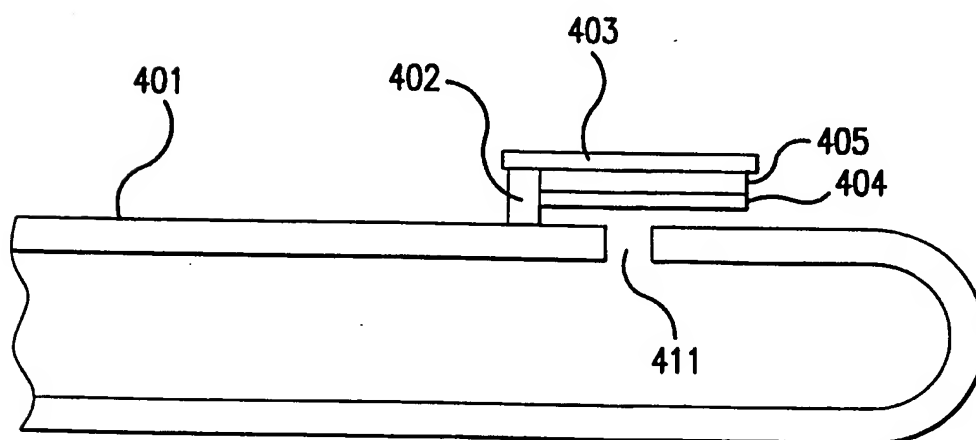


FIG. 12

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/17526

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D11/00 B65D33/34

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 407 277 A (KCL CORP.) 18 April 1995 (1995-04-18) claims; figure 2 column 3, line 15 ---	1
A	GB 2 123 791 A (DRG INC.) 8 February 1984 (1984-02-08) abstract page 1, line 67-71 ---	1
A	US 4 028 118 A (PILOT INK CO.) 7 June 1977 (1977-06-07) abstract column 7, paragraphs 4,6 column 8, paragraph 3 column 12, line 31-36 column 13, line 18-25 ---	12, 17, 25
-/--		



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

26 September 2000

Date of mailing of the international search report

06/10/2000

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PCT/US 00/17526

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 527 385 A (SAKURA COLOR PRODUCTS CORP.) 18 June 1996 (1996-06-18) abstract column 1, paragraph 1 ---	12, 17
A	FR 2 649 078 A (BROSSIER MICHEL) 4 January 1991 (1991-01-04) claims 1-6 -----	1

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Information on patent family members

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